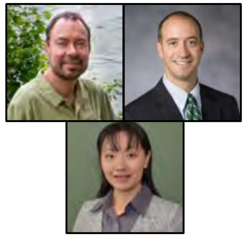
NC PFAS Testing Network Research Objectives

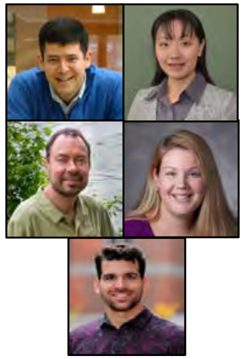


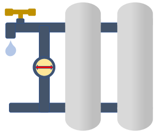
(1) Statewide Baseline Water Testing

- ✓ measure PFAS levels by targeted analysis
- ✓ estimate total organic fluorine
- ✓ identify more PFAS with non-target analysis

(2) Private Well Contamination Risk Modeling

- ✓ calculate time for PFAS to flush from aquifer
- ✓ analyze contributions to well contamination
- ✓ create app for private well owners to predict risk





(3) PFAS Removal Performance Testing

- ✓ evaluate commercial options
- ✓ test tap water with in-home filtration
- ✓ develop and test novel Fluorogel materials
- ✓ assess electrochemical degradation

(4) Air Emissions & Atmospheric Deposition

- ✓ identify PFAS present in air and rainwater
- ✓ analyze geographic distribution of PFAS
- ✓ calculate contribution of wet dep. to watershed
- ✓ investigate multiphase atmospheric chemistry

(5) Applied Research Projects

- ✓ assess importance of other PFAS sources (landfills, wastewater) to POTWs and surface waters

- ✓ study PFAS bioaccumulation and biomagnification in ecologically relevant species

- ✓ test PFAS in mouse model of immunotoxicological response

- ✓ examine PFAS uptake in food crops and effects of soil composition

- ✓ study effects of PFAS on pregnancy and placental health and function

- ✓ develop mathematical models to predict where PFAS go in organisms and the environment

- ✓ Create a statewide inventory of PFAS-containing firefighting foams and make recommendations for collection and disposal

Team 1: Statewide Baseline Testing of Public Water Sources

Milestones

- Completed Round 1 (376 samples) targeted analysis (~50 PFAS); Round 2 ongoing
- Completed AOF analysis of Round 1 water samples for comparison with targeted results (mass balance)
- Non-target high resolution analyses ongoing (Round 1 samples run by HRMS, data analysis has started)

Results suggest

- Of the 376 water sources tested in round 1, 20 had ΣPFAS $\geq$ 70 ng/L (max 425 ng/L), 71 had ΣPFAS 10-70 ng/L, and 285 had ΣPFAS < 10 ng/L
- 9/10 sources with the highest PFAS concentrations were in the Cape Fear River basin
- 8/10 sources with the highest PFAS concentrations were impacted by fluoroethers
- GenX was not detected above 140 ng/L, but 3 fluoroethers were (PFMOAA, PFO2HxA, PMPA)
- PFOA+PFOS exceeded 70 ng/L in 2 sources (one has since been taken out of service, and the other is treated with activated carbon to bring PFOA+PFOS to below 70 ng/L in the finished drinking water)
- Important PFAS sources are the Fayetteville Works site (Chemours), AFFF, municipal wastewater, and runoff from fields that received biosolids
- PFAS molecular profiles vary among drinking water sources, highlighting complex mixtures created by multiple sources.
- Adsorbable organic fluorine (AOF) was below the method reporting limit of 400 ng/L for 89% of tested sources and >2000 ng/L (max. 6,700 ng/L) in 2% of sources tested in round 1

Recommendations

- Testing should be expanded to include additional groundwater sources to capture spatial variability among wells
- Testing should continue to capture temporal variability of impacted sources (e.g. Pittsboro had 54 ng/L in round 1 and 840 ng/L in round 2)
- Toxicological studies are needed for the compounds that are (1) most frequently detected and (2) detected at the highest concentrations
- Toxicological studies should consider that PFASs occur in mixtures
- AOF is a good screening tool for prioritizing samples for non-target analysis

Team 2: Private Well Contamination Risk Modeling

Milestones

- Built a database of multiple factors that might influence GenX in well water (1,207 wells, 422data types)
- Applied artificial intelligence algorithms and cross-validated predictive model
- Developed prototype Web application for users to predict contamination of untested wells
- Published results in *Journal of Hazardous Materials*
- Quantified PFAS discharge from groundwater to streams near Chemours, preliminary constraint on flushing times

Results

- Risk can be predicted, even with limited data on well characteristics
- Baseflow discharge of PFAS from groundwater (gw) to streams near Chemours about 32 kg/yr
- No PFAS-free gw below streams, higher PFAS in younger gw but even oldest sample (29 yr, recharged in 1990, 10 yr after start of emissions) had 91 ng/L GenX, short chain PFAS moving through gw to streams quickly (couple decades)

Recommendations

- Establish monitoring stations on streams near Fayetteville Works (flow, PFAS concentration)
- Further work with PFAS and gw age-dating, better constrain PFAS flushing times for wells and tributary watersheds
- Conduct additional private well testing in areas at highest risk (northwest, northeast of Chemours)

Team 3: PFAS Removal Performance Testing

Milestones

- Evaluated GAC, IEX resins, and high-pressure (RO/NF) membranes in bench scale experiments for PFAS removal
- Tested effectiveness of POU treatments for residential removal of PFAS
- Developed novel ionic fluorogel resin for PFAS removal and compared to existing technologies
- Optimized electrochemical degradation method for PFAS destruction

Results suggest

- **Activated carbon:** rapid small-scale column tests that can be completed in 4 days can effectively predict PFAS removal in granular activated carbon adsorbers used in drinking water treatment plants; reagglomerated, coal-based activated activated carbons are most effective for PFAS removal; dissolved organic carbon adversely affects PFAS removal
- **Ion exchange resins:** the resin polymer type is the most important factor for PFAS removal, with multiple PS-DVB resins on the market capable of effectively removing most PFAS structures.
- **Novel ionic fluorogel**: a platform approach for the development of ionic fluorogel (IF) resins that effectively remove a chemically diverse mixture of PFAS from water was developed. The IF resin contains fluorous and ionic components that provide the IF specificity for removal of PFAS over background organic matter.
- **Membranes:** commercially available high-pressure membranes are an effective treatment technology for PFAS removal. The membranes used in this study achieved PFAS rejection levels in the ~50% to 99.9% range. Greater variability in rejection was observed with lower molecular weight (i.e. ≤300 g/mol) PFASs. There were no clear associations between membrane rejection efficacy and PFAS functional group.
- **Electrochemical processes:** electrochemical destruction can remove >80% PFOA and >60% GenX, with some mineralization but also generation of unknown organic fluorinated end products.
- **Point-of-use (POU) systems:** common activated carbon based POU water filters (e.g. pitcher filters and in-line refrigerator filters) did not completely remove PFAS and displayed a wide range in removal efficiency. Generally, longer chain PFAS were removed more efficiently than shorter chain PFAS. Some filters displayed signs of saturation and appeared to be sources of PFAS to the tap water. POU reverse osmosis and two-stage filters performed very well in removing PFAS (~>99%)

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Recommendations

- **Activated carbon:** dissolved organic carbon removal prior to activated carbon treatment should be optimized to improve PFAS removal efficiency, disposal/reuse options for spent activated carbon need to be explored in future studies
- **Ion exchange resins:** Resins need to be changed frequently if short-chain PFAS are present, and disposal of exhausted resins need to be further explored since regeneration without significant fraction of organic solvents is ineffective for PS-DVS resins.
- **Novel ionic fluorogel:** ionic fluorogel resins are a promising novel material for removal of PFAS from water. Further evaluation of the IF resins in flow-through and upscaled systems is needed to evaluate their applicability as a complement to or replacement for existing PFAS removal technologies.
- **Membranes:** high-pressure membranes reduce PFAS presence in drinking water, with *tighter* membranes (RO instead of NF) exhibiting higher efficacy in PFAS removal. Membrane selection should strike a balance between needed PFAS removal and water productivity for each use scenario (e.g., community water treatment plant, home system, water source, etc.)
- **Electrochemical processes:** During electrochemical treatment, gas emission control is important to prevent significant PFAS transport into the aerosol phase.
- **Point-of-use (POU) systems:** While not all POU filters are 100% effective, any filter will help remove PFAS and therefore reduce PFAS exposure; however, routine maintenance and frequent exchange of cartridges are recommended to ensure that filters do not saturate.

Team 4: PFAS in Air Emissions and Atmospheric Deposition

Milestones

- Statewide ***ambient air*** PFAS Concentration Measurements; quarterly concentrations for 1 year ($PM_{2.5}$)
- ***Airborne*** PFAS Concentrations upwind and downwind of Chemours. (near-field, within 1.5 km)
- Statewide ***wet/dry deposition*** over winter/summer 2019
- ***Wet deposition*** on event basis and ***dry deposition*** twice a month in Wilmington for 1 year (2019)

Results suggest

- Of 34 ***ambient air*** PFAS measured statewide, only PFOS and PFOA were >1pg/m3, all during July-Sept
- In ***air***, more compounds were >1pg/m^3 within 1.5 km of Chemours
- ***Wet deposition*** is more efficient at scavenging PFAS from the atmosphere than dry deposition
- No impact of air mass origin on ***deposition*** concentrations or flux
- Legacy PFAS are present ***in air and deposition*** even though production has been phased out

Recommendations

- Investigate atmospheric partitioning/deposition with synchronous aqueous-, particle-, and gas-phase samples
- Better constrain atmospheric PFAS sources through source tracking (e.g. isomers)
- Study atmospheric transformations of PFAS to better understand sources and predict concentrations (in lab)
- Measure PFAS indoors, a major exposure location

Team 5a: PFAS in Landfill Leachate and Wastewater

Milestones

- Sampled 16 MSW and 5 construction and demolition (C&D) waste landfills; 31 wastewater treatment plants (WWTPs) (influent and effluent)
  - captured 37% of statewide WWTP design flow rate
- Considered release to 17 North Carolina river basins

Results suggest

- The extent to which landfill leachate is a significant contributor to wastewater influent is site-specific
- In some cases, treatment at a landfill may be optimal while treatment at the wastewater plant may be optimal in other cases

Recommendations

- Emphasize mass release as opposed to concentrations; require annual leachate flow data in annual reports
- Encourage partnerships between WWTPs and landfills
- Identify non-domestic sources of PFAS in wastewater influent and assess appropriateness of pre-treatment
- Quantify the release of volatiles from WWTPs
- More review and regulation of unlined landfills containing C&D waste is needed as these sites are PFAS sources
- Allow for site-specific management in consideration of the watershed
- Support is needed to facilitate facility sampling

Team 5b: Ecotoxicological Effects of PFAS (Striped Bass & Alligators)

Milestones

- Collected and analyzed blood/serum of striped bass (n=58) from Cape Fear River and compared to controls (n=29) raised in Pamilco Aquaculture lab (results published: Environment International 135 (2020) 105358).
- Compared exposures and health outcomes of CFR Alligators to that of low-exposure controls from Lumbar Watershed.
- Expanded the SAFEwaterNC Study to include angler's questionnaire and evaluation of PFAS in consumed fish.

Results suggest

- PFAS were detected in every sample with PFOS, PFNA, PFDA detected in every Striped Bass.
- Nafion BP2 was only detected in CFR samples (78%); GenX (50%) and PFHxS were highly enriched in CFR samples.
- PFOS accounted for 89% of targeted PFAS present in serum of Striped Bass from CFR.
- Differential accumulation was observed between Striped Bass serum and filet.
- PFAS exposure is associated with biomarkers of adverse effects on liver and immune function in CFR Striped Bass.
- In the Alligator study, an exposure gradient was observed in the Cape Fear River (downstream of manufacturing)

Recommendations

- Continue studies to measure PFAS exposure, bioaccumulation and biomagnification in consumed fish
- Continue evaluation of autoimmune effects in Alligators at Greenfield Lake

Team 5c: Immunotoxicological Responses of PFAS in mice

Milestones

- Completed 30-day in vivo immunotoxicity studies with PFMOAA ($C_3HF_5O_3$), PFMOPrA ($C_4HF_7O_3$), PFMOBA ($C_5HF_9O_3$), Nafion Byproduct 2 ($C_7H_2F_{14}O_5S$)
- Completed 30-day repeat in vivo studies of PFMOAA and Nafion Byproduct 2 (partly with funds from another award)*
- Completed 15-day in vivo study of PFMOAA mixed with Nafion Byproduct 2 (partly with funds from another award)*

Results suggest

- At the doses administered, PFMOAA, PFMOPrA, and PFMOBA do not appear to produce overt toxicity and only mild immunotoxicity (no to minimal suppression of antibody production)
- At the doses administered, Nafion Byproduct 2 appears to be overtly toxic and produced profound immunotoxicity
- Mixture study data evaluation is ongoing, but the PFMOAA-Nafion Byproduct 2 mixture appears to produce greater overt toxicity than the individual compounds alone

Recommendations

- Additional mixtures studies to better understand how these PFAS may influence on another
- Evaluation of urinary concentrations to estimate biological half-lives (blood concentrations were low)
- Focus on molecular changes associated with antibody suppression compared to changes induced by legacy PFAS

*Plan was to evaluate six different PFAS; funds from other award were necessary to complete these repeat studies due to increases in animal costs, personnel costs, and other supplies.

Team 5d: PFAS Uptake in Food Crops and Effects of Soil Composition

Milestones

- Completed greenhouse study and analysis to determine impact of compost additions on PFAS uptake by lettuce
- Completed greenhouse study to determine PFAS uptake by cucumbers, carrots, celery, and sweet potatoes from contaminated soil (analysis pending)

Results suggest

- The fluoroether compounds GenX and PFMOAA are transported to leaves to a greater extent than the legacy compounds PFOS and PFOA
- Adding uncontaminated compost to soil dramatically reduces the uptake of PFAS by lettuce

Recommendations

- Additional plant uptake studies, including those still in progress (see Milestones), are needed to evaluate plant species differences and translocation of PFAS to seed and fruit
- Additional studies should probe the occurrence of PFAS in other foods
- Exposure models should incorporate diet in their assessment
- Biosolids and irrigation water should be evaluated for their possible contribution of PFAS to agricultural products

Team 5e: PFAS Effects on Pregnancy and Placental Health

Milestones

- Monitored 122 placentas from high-risk pregnancies (UNC Hospital Preterm Biobank Study) for levels of 26 PFAS.
- Analyzed 68 drinking water samples from participants for 12 PFAS.
- Measured response (trophoblast migration and invasion) of placental cells to PFAS treatment in vitro and examined the cellular pathways displaying altered gene expression (panel of 91 inflammatory genes expressed in the human placenta and involved in preeclampsia, cellular movement, or both and genes regulating invasion of trophoblasts).

Results suggest

- In the placenta, 11 PFAS were detected in at least one sample; only 4 PFAS were detected above LOD in at least 50% of samples (PFOS >> PFHxS > PFUnA > PFHpS). None of the PFAS were associated with detrimental pregnancy health outcomes in this UNC-Chapel Hill cohort.
- In drinking water, PFHxA and PFHpA were the most frequently detected, PFHxA and PFPeA had the highest concentrations, and 6 PFAS (PFHxS, PFNA, PFOS, PFDA, PFUdA, GenX) were not detected.
- In placental cells, PFOS, PFOA, and GenX decreased the rate of trophoblast migration (27.9%, 19.3%, and 31.2%) and GenX decreased trophoblast invasion ~3-fold over PFOS (37.5% vs. 11.1%) while PFOA had no effect.
- In placental cells, of the 91 inflammatory genes measured, 23 were significantly altered by one or more PFAS and represented 4 categories: chemokines, chemokine receptors, chemokine ligands, and enzymes.
- In placental cells, both PFOS and PFOA significantly inhibited transcription of matrix-metalloproteinase 2 (MMP2), and PFOS alone inhibited that of MMP9.

Recommendations

- Suggest scanning drinking water for PFAS among pregnant women in NC.
- Investigate the effects of PFAS on trophoblast stem cell differentiation in vitro.
- Measure PFAS-induced gene expression changes ex vivo using human placental explants.
- Determine the mechanistic target of PFAS in trophoblast cells.

Team 5f: PFAS Benchmark Dose Modeling

Milestones

- Initial experimental data (8/2019) was not conducive to modeling efforts. Recent findings (1/2021) may be more suitable for Benchmark Dose Modeling. Efforts to construct model and analyze data are ongoing.
- Examined previously published modeling efforts for PFAS.
- Supervised a pair of undergraduate research students (as part of the NCA&T/Elon Joint REU in Mathematical Biology) who investigated a PBPK model for PFOS and PFOA and searched for optimal parameters to fit the model to previously published data.

Results suggest

- Efforts are ongoing.

Recommendations

- To be determined.

Other: Collaboratory Firefighting Foam Inventory

Milestones

- Qualtrics survey was developed and sent to 100 NC County Fire Marshals to forward to Fire Departments
- Office of the State Fire Marshal sent memo to County Marshals urging their participation
- Follow-up survey was sent to approx. 1400 individual Fire Chiefs/Captains

Results suggest

- Low participation: concerns about the study and how the data will be used
- Many stations are not using PFAS-containing AFFF and some don’t know what they have
- Stations would like to know how to get rid of unwanted foams

Recommendations

- Annual review and update of fire departments directory including points of contact
- Implement a user-friendly tracking system for stations to report AFFF deployment in training or emergencies
- Collect additional inventory data to determine the amount of PFAS-containing AFFF to be disposed
- Alternatives to PFAS-containing AFFF should be used in all firefighting training
- Baseline biomonitoring of PFAS in firefighters exposed through AFFF and protective gear